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## Alkali-metal stoichiometry and structure of $K_4C_{60}$ and $Rb_4C_{60}$

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Alkali-metal fulleride samples  $K_xC_{60}$  and  $Rb_xC_{60}$  with stoichiometries close to  $x=4$  were examined with x-ray powder-diffraction measurements at room temperature. We have shown through Rietveld refinements that  $A_4C_{60}$  is a line phase with charge per lattice site that is closer to integer than in any other fulleride. The  $C_{60}$  molecules are disordered between two possible orientations within the body-centered-tetragonal lattice with the three orthogonal twofold rotation axes aligned with the unit-cell translation vectors in space group  $I4/mmm$ . The x-ray diffraction results exclude any quadrupole distortion of the fullerene molecule beyond about 0.04 Å. These results suggest that  $K_4C_{60}$  and  $Rb_4C_{60}$  may be Mott insulators. [S0163-1829(97)51806-6]

The wide range of electronic phenomena in alkali-metal fullerides and the connection between their structural and electronic properties have been a rich field of interest.<sup>1</sup> Briefly, body-centered-cubic (bcc)  $A_6C_{60}$  and body-centered-tetragonal (bct)  $A_4C_{60}$  are insulators, and fcc  $A_3C_{60}$  and  $AC_{60}$  are conductors, with the former becoming a superconductor at low temperature and the latter exhibiting various phases with interfullerene chemical bonds. In the simplest view, electrons donated by the alkali-metal atoms are transferred to the six available  $t_{1u}$   $C_{60}$  molecular orbitals. The conductivity of fcc  $A_3C_{60}$  and  $AC_{60}$  follows from this partially filled band, whereas the mechanism leading to the insulating nature of  $A_4C_{60}$  is still unclear.

At the outset, one might think that  $A_4C_{60}$  is an insulator because the tetragonal structural symmetry splits the conduction band, thereby creating a gap. However, detailed band structure calculations predict that  $K_4C_{60}$  is a metal.<sup>2</sup> The situation is actually complicated by the fact that the electron correlation energy significantly exceeds the bandwidth.<sup>3</sup> It is well known that a sufficiently large electron correlation energy will make any system with a partially filled band a Mott-Hubbard insulator if there is an integer number of electrons per lattice site. In the (super)conducting nominal  $A_3C_{60}$  phase, a significant concentration of alkali-metal vacancies has been found, resulting in an electrons-per-fullerene ratio of  $m = 2.93 \pm 0.03$ .<sup>4,5</sup> However, it has not been possible to control the off-integer doping of that phase. It is therefore interesting to study the precise stoichiometry of  $A_4C_{60}$  and its doping dependence on the coexistence of other phases, in the hope of elucidating its electronic properties.

The photoemission spectra<sup>6</sup> exhibit a lack of states at the Fermi surface suggestive of a Mott-Hubbard-type insulator, and muon spin resonance<sup>7</sup> shows that the material is a non-magnetic insulator. Magnetization<sup>8</sup> and <sup>13</sup>C NMR (Ref. 9) measurements confirm this result, and provide estimates of the electronic gap and fullerene reorientation energies. Previous work identified the rough structure of  $A_4C_{60}$  as body-centered tetragonal approximating the  $C_{60}$  molecules by spherical shells of charge.<sup>10</sup> We have performed a much

more detailed structural study of  $K_4C_{60}$  and  $Rb_4C_{60}$ , particularly emphasizing the stoichiometry of these phases.

The preparation of the samples  $K_xC_{60}$  and  $Rb_xC_{60}$  with  $x \approx 4$  was carried out in two steps. First,  $C_{60}$  powder with nominal purity 99.97% was vacuum sublimated and reacted at 250 °C with an appropriate amount of potassium or rubidium metal in order to get an overdoped sample  $A_{4.5}C_{60}$ . This sample was annealed for 7–20 days at 450 °C in sealed, evacuated ( $\approx 4 \times 10^{-6}$  Torr) glass tubes. In the second step of the preparation, subsequently the  $A_{4.5}C_{60}$  was diluted with  $C_{60}$  powder, reground, and annealed at 450 °C for 10–40 days. The compositions of the samples were measured via x-ray diffraction at different steps of the preparation process.

The x-ray powder-diffraction measurements were carried out on beamline X3B1 of the National Synchrotron Light Source at Brookhaven National Laboratory. X-rays of wavelength 1.15 Å were selected by a double crystal Si(111) monochromator, and were then analyzed by a Ge(111) crystal providing high angular resolution. On an  $Al_2O_3$  reference standard, we typically observe peaks with full width at half maximum on the order of 0.02° in scattering angle  $2\theta$ . This is much narrower than any peak observed from the present samples.

Our goal was to produce phase-pure samples of  $A_4C_{60}$  and to explore the range of stoichiometry possible for this phase. However, we were unable to prepare samples without a trace of either fcc  $A_3C_{60}$  or bcc  $A_6C_{60}$ . This is illustrated in Fig. 1 which shows details of x-ray patterns of the over- and underdoped Rb samples with the least amount of coexisting phases. For a short anneal of 5 days, the coexistence of three phases was observed: fcc  $A_3C_{60}$ , bct  $A_4C_{60}$ , and bcc  $A_6C_{60}$ . This never occurred for bakes longer than 14 days; only two coexisting phases were then observed, which is an indication that the samples had reached equilibrium.<sup>11</sup>

The difficulty in obtaining phase-pure samples of  $A_4C_{60}$  stands in stark contrast to previous work on  $Rb_3C_{60}$  and  $Rb_6C_{60}$ . There, it has been possible to produce phase-pure

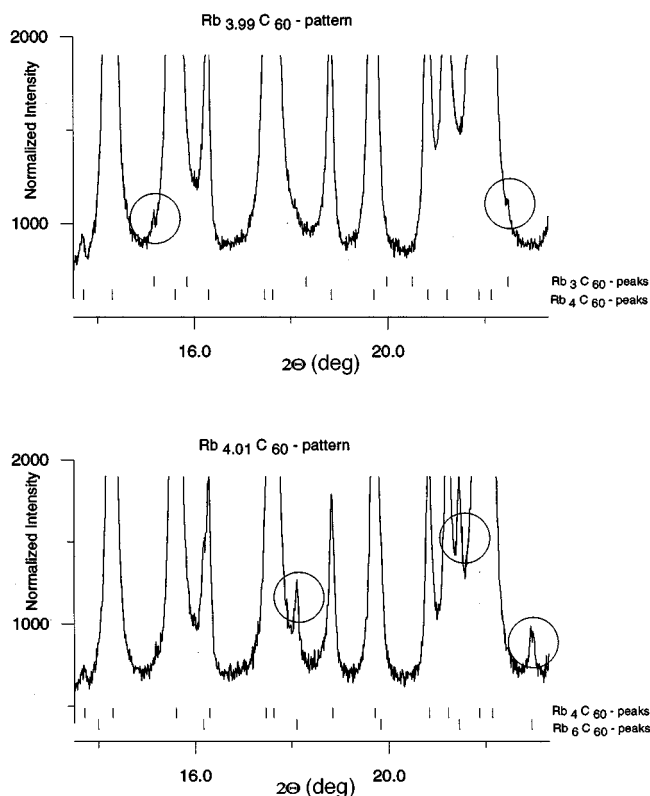


FIG. 1. Details of the x-ray patterns of Rb samples with the least amount of coexisting phases. The maximum normalized intensity is 23 000 for  $\text{Rb}_{3.99}\text{C}_{60}$  and 16 500 for  $\text{Rb}_{4.01}\text{C}_{60}$ .

samples of the fcc, nominally  $\text{Rb}_3\text{C}_{60}$  phase over a range of nominal stoichiometry,<sup>4</sup> and a bcc phase  $\text{Rb}_x\text{C}_{60}$  has been observed with  $x$  significantly less than 6 and with lattice parameter significantly smaller than in the saturated  $x=6$  phase.<sup>12</sup> While differences in sample preparation, diffusion rates, nucleation barriers, etc. make it difficult to reach a definitive conclusion from this observation alone, it does suggest that  $\text{K}_4\text{C}_{60}$  and  $\text{Rb}_4\text{C}_{60}$  are line phases, with smaller tolerances for vacancies than other fullerides.

We have used standard Rietveld<sup>13</sup> techniques to analyze the diffraction patterns of four  $\text{K}_x\text{C}_{60}$  samples with actual stoichiometries in the range  $x=3.68-4.12$ , and five  $\text{Rb}_x\text{C}_{60}$  samples with  $x=3.95-4.13$ . These stoichiometries were determined by x-ray pattern analysis, carried out in two stages. The first was a profile matching step, introduced by LeBail,<sup>14</sup> with unit-cell parameters, profile shape parameters and the individual Bragg intensities varied independently without referring to any structural model. The quality of fit is gauged by the weighted profile  $R$ -factor  $R_{wp}$ , which is defined in any standard reference.<sup>13</sup> The LeBail fit provides a lower bound on  $R_{wp}$  achievable in the structural refinement. In the second stage, the Rietveld analysis, we have refined the position, fractional occupancy of the alkali-metal and the isotropic thermal parameters of the alkali-metal and carbon atoms, holding the unit-cell and profile shape parameters fixed to the values obtained by the LeBail fit. A typical Rietveld refinement, that of  $\text{K}_{4.12}\text{C}_{60}$  ( $R_{wp}=5.82$ ), is shown in Fig. 2. This uses space group  $I4/mmm$  with merohedral disorder of the fullerenes, similar to  $\text{K}_3\text{C}_{60}$ .<sup>15</sup> The corresponding LeBail fit gives  $R_{wp}=5.04$ ; the discrepancy between the

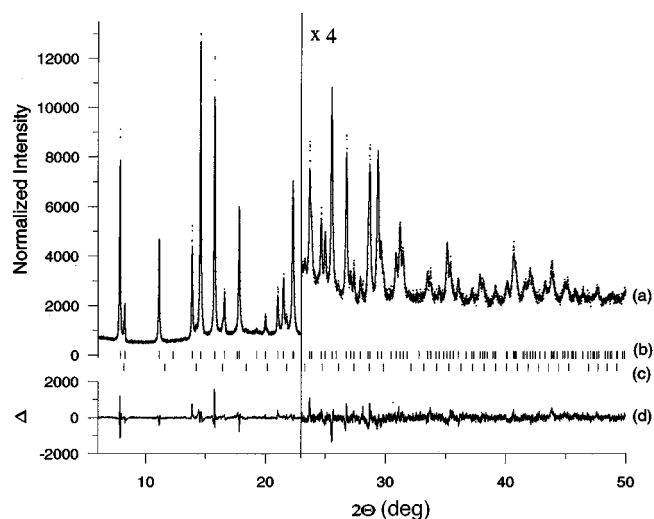


FIG. 2. Room temperature x-ray diffraction pattern of the  $\text{K}_{4.12}\text{C}_{60}$  sample with the Rietveld fit ( $R_{wp}=5.82$ ) to the profile. Trace (a) is the raw data and best fit profile, (b) and (c) indicate peak positions for  $\text{K}_4\text{C}_{60}$  and  $\text{K}_6\text{C}_{60}$ , respectively, and (d) is the difference (data fit).

quality of the Rietveld and LeBail fits is within the range of typical experience for a correct structural model.

We have compared various models for the placement of the fullerene in the lattice.<sup>16</sup> As suggested by previous work,<sup>17</sup> the best fit was obtained with the fullerenes disordered between the two standard orientations, defined by the alignment of three orthogonal twofold axes with the unit-cell translation vectors. Furthermore, we have considered other orientations, e.g., fullerenes rotated from the standard orientation by  $45^\circ$  about the  $c$  axis, and found that the quality of fit becomes much worse. This is consistent with alkali-metal-carbon distance calculations:<sup>16</sup>  $\text{C}_{60}$  rotation away from the standard orientations decreases the minimum alkali-metal-carbon distances to unphysically small values.

The refined structural parameters of the Rietveld analyses are given in Table I. The listed compositions were derived from the refined scale factors of the coexisting phases. The radius of the fullerene was refined to 3.56 Å. It is generally observed that the estimated standard deviations of param-

TABLE I. Refined parameters of the bct phase  $\text{K}_4\text{C}_{60}$  and  $\text{Rb}_4\text{C}_{60}$  and corresponding  $R_{wp}$  factors. Numbers in parentheses are estimated standard deviations, corrected according to the method of Scott (Ref. 18).

| Refined comp.                   | $a$ [Å]   | $c$ [Å]   | $N$       | $(x, \frac{1}{2}, 0)$ | $R_{wp}$ |
|---------------------------------|-----------|-----------|-----------|-----------------------|----------|
| $\text{K}_{3.68}\text{C}_{60}$  | 11.864(1) | 10.761(2) | 1.008(18) | 0.211                 | 6.73     |
| $\text{K}_{3.87}\text{C}_{60}$  | 11.864(1) | 10.760(2) | 1.002(12) | 0.211                 | 6.53     |
| $\text{K}_{3.99}\text{C}_{60}$  | 11.867(1) | 10.765(2) | 0.990(15) | 0.211                 | 6.46     |
| $\text{K}_{4.12}\text{C}_{60}$  | 11.864(1) | 10.761(2) | 0.985(10) | 0.211                 | 5.82     |
| $\text{Rb}_{3.95}\text{C}_{60}$ | 11.967(1) | 11.011(1) | 0.997(13) | 0.215                 | 6.41     |
| $\text{Rb}_{3.95}\text{C}_{60}$ | 11.969(1) | 11.013(2) | 0.995(16) | 0.215                 | 6.43     |
| $\text{Rb}_{3.99}\text{C}_{60}$ | 11.969(2) | 11.017(1) | 0.996(13) | 0.214                 | 6.12     |
| $\text{Rb}_{4.01}\text{C}_{60}$ | 11.966(1) | 11.015(1) | 0.988(18) | 0.215                 | 6.03     |
| $\text{Rb}_{4.13}\text{C}_{60}$ | 11.962(1) | 11.018(2) | 0.994(18) | 0.215                 | 6.44     |

eters calculated by Rietveld analysis are too small. They measure the statistical variation (precision) rather than the discrepancy from the correct value (accuracy). Therefore, we applied the correction suggested by Scott.<sup>18</sup> The refined fractional alkali occupancies  $N$  in Table I vary slightly from unity. In order to judge with confidence whether these deviations are statistically significant, we have compared Rietveld refinements with  $N$  fixed at unity with those for which it is allowed to vary. According to standard statistical methods, the likelihood that an improvement of the quality of fit due to the introduction of one or more additional parameters is significant can be computed as the  $F$  statistic. We applied this significance test to the refined  $N$  of  $K_{4.12}C_{60}$ , because it exhibits the largest discrepancy from unity. Here, the fractional potassium occupancy refines to  $N=0.985\pm 0.010$  with  $R_{wp}=5.82$ , with altogether 16 refined parameters and 85 distinct Bragg reflections. If  $N$  is fixed at unity, the weighted  $R$  factor increases to  $R_{wp}=5.84$ . This gives an  $F$  ratio  $F=0.668$ ,<sup>19</sup> implying that there is a likelihood of about 65% (Ref. 20) that the difference is purely a statistical fluctuation. In view of the fact that the other samples have a far smaller deviation from unity, we conclude that all samples are within 1% of their ideal alkali-metal to fullerene ratio of 4. This may be compared to the deficiency of more than 2% observed for  $K_3C_{60}$  and  $Rb_3C_{60}$ .<sup>4</sup>

The insulating behavior of  $A_4C_{60}$  could also arise from a Jahn-Teller distortion of the fullerene molecules, splitting the sixfold degenerate  $t_{1u}$  molecular orbital enough to produce a gap in the conduction band. This would produce a quadrupole distortion of the fullerene,<sup>21</sup> which would presumably be aligned to the tetragonal crystal field. It is not possible to refine the position of each carbon atom on the fullerene, but we can describe a hypothetical ellipsoidal distortion through factors  $\sigma_{xy}$  and  $\sigma_z$ , so that each carbon atom is moved from its rigid fullerene position of  $(x,y,z)$  to  $(\sigma_{xy}x, \sigma_{xy}y, \sigma_z z)$ .

Rietveld refinement of these distortion factors did not improve the quality of fit for either potassium or rubidium. In order to determine the maximum possible distortion consistent with the data, we examined the increase of  $R_{wp}$  as a function of  $\sigma_{xy}$  and  $\sigma_z$ . For example, consider the  $K_{3.99}C_{60}$  sample listed in Table I. According to the  $F$  statistic, a degradation of  $R_{wp}$  from 6.46 to 6.59% is statistically significant at the 95% confidence level, i.e., the probability is only 5% that the quality of fit degrades to this level by chance. The contour plotted in Fig. 3 traces the values of  $\sigma_{xy}$  and  $\sigma_z$  which produce  $R_{wp}=6.59\%$ . Distortions  $(\sigma_{xy}, \sigma_z)$  outside the ellipse are excluded by the data.

Our experimental results can be summarized as follows. The vacancy concentration in both  $K_4C_{60}$  and  $Rb_4C_{60}$  is significantly less than what is observed in conducting  $K_3C_{60}$  and  $Rb_3C_{60}$ . Together with the experience that it is extremely difficult to obtain a pure  $A_4C_{60}$  sample, we conclude that this is a line phase with charge per lattice site which is closer to integer than in any other fulleride. Furthermore, we find that the fullerenes are spherical, and place a limit of 0.04 Å on the difference between equatorial and polar radius.

We now proceed to consider the implications of these results towards an understanding of the physical behavior of the fullerides. Several possibilities have been proposed in order to explain the difference between insulating  $A_4C_{60}$  and

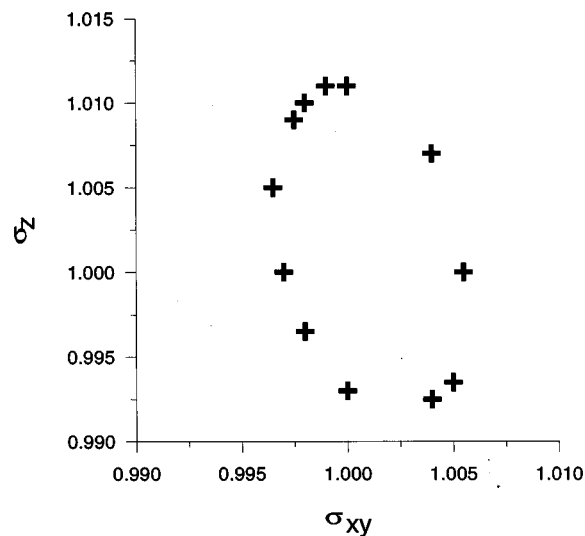


FIG. 3. Contour plot for  $(\sigma_{xy}, \sigma_z)$  distortions with  $R_{wp}$  corresponding to a 95% confidence level; values  $(\sigma_{xy}, \sigma_z)$  outside the ellipse provide a significantly worse fit. For the Rietveld analysis the  $K_{3.99}C_{60}$  pattern has been used.

conducting  $A_3C_{60}$ : band theory, charge density wave, Mott insulator, and Jahn-Teller distortion. Band theory predicts that  $A_4C_{60}$  is a metal, although the orientational disorder is a subtlety not taken into account.<sup>2</sup> If a charge density wave state is responsible for the insulating behavior, one would expect that it would be destroyed at elevated temperatures. However,  $K_4C_{60}$  remains an insulator to at least 480 K.<sup>9</sup>

Either a Mott insulator or a Jahn-Teller distortion is consistent with the recent NMR observation that  $Rb_4C_{60}$  becomes metallic as the pressure is increased.<sup>22</sup> The application of pressure increases the bandwidth, which would drive either a Mott insulator or a Jahn-Teller system into a conducting state. Likewise, both interpretations are consistent with the observation of a nonmagnetic ground state.<sup>7-9</sup> Previous theoretical discussions of the likelihood of a Jahn-Teller distortion in  $A_4C_{60}$  have not reached a consensus.<sup>23,24</sup> It is not clear *a priori* how large a Jahn-Teller distortion would be expected. We hope that this will motivate accurate calculations along the lines of the electron-phonon coupling constant in  $A_3C_{60}$ .<sup>25,26</sup> It has also been argued that there are significant quantum effects in the coupling of the  $C_{60}$  LUMO to quadrupole vibrations.<sup>21</sup> Another possibility, that  $A_4C_{60}$  is an insulator due to electron-electron correlations, has been noted several times.<sup>9,6,27</sup> The present work adds some weight to that suggestion by showing a clear difference between an insulator ( $A_4C_{60}$ ) with integer charge per fullerene and a conductor ( $A_3C_{60}$ ) doped by cation vacancies.

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